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A Laboratory Study of Nitrogen Fixation in the High Tension Arc

by

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A LABORATORY STUDY OF NITROGEN FIXATION IN THE HIGH TENSION ARC*

Because of the interest in the utilization of cheap hydroelectric power in the Northwest for the fixation of atmospheric nitrogen by the arc process, some experimental work has been carried on in this laboratory. A portion of the results are presented herein and deal mainly with (1) the effect of pressure on the yield of fixed nitrogen, (2) the equilibria obtained with various mixtures of nitrogen and oxygen and (3) the effect of moisture on the yield when air is used.

An extensive review of the literature on the fixation of nitrogen need not be given here. Investigations on the effect of pressure on the oxidation of nitrogen by means of the alternating current arc are not numerous.[2] Practically no quantitative data have been reported on the effect of reduced pressure of this type of arc operating with *good energy efficiency* (shown by yield of fixed nitrogen) at atmospheric pressure. For long the question has been in the minds of investigators as to whether the reaction between nitrogen and oxygen as obtained from the electric arc may be represented as typical reversible reactions conforming to the law of mass action[3]. Published data are not available giving the results of properly determined equilibria using different mixtures of nitrogen and oxygen with arcs operating under conditions necessary for a good yield of fixed nitrogen. Lastly, the literature dealing with the effect of moisture on the oxidation of nitrogen in air by means of the electrical discharge, is both meagre and conflicting[4]. In fact, no extensive quantitative data are available.

Description of Apparatus

(a) *Electrical Equipment*

The power available was a 110 volt, 60 cycle, alternating current. An air-cooled, closed-core transformer of three and one-half kilowatts capacity, was used to give the high tension current. The transformer was calibrated for both resistance and core losses. An adjustable reactance was used to stabilize the arc and control the electrical conditions.

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* Contribution from the Chemistry Department of the University of Washington.

[1] Du Pont Fellow in Chemistry at the University of Washington, 1921-1923.

[2] Haber et al: Z. Elektrochem., **13**, 725 (1907); **14**, 689 (1908); **16**, 789, 796 (1910); Briner and Naville: Helv. chim. acta, **2**, 348 (1919); J. Chim. phys., **17**, 329 (1919); Final Report Nitrogen Products Committee (British), p. 241 (1920).

[3] See Knox: "Fixation of Atmospheric Nitrogen", pp. 7-36 (1921) for review of literature prior to 1920; Steinmetz: Chem. & Met. Eng., **22**, 299, 353, 411 (1920); Daniels, Keene and Manning: Trans. Am. Electrochem. Soc., **44**, 247 (1923).

[4] Warburg and Leithäuser: Ann. Physik, (4) **20**, 743 (1906); Sapozlinikov, Guidima and Kotovi: J. Russ. Phys. Chim. Soc. **45**, 1076 (1913); Briner and Naville: J. Chim. phys. **17**, 329 (1919); Final Report Nitrogen Products Committee (British), p. 241 (1920); Gros: Compt. rend. **170**, 811 (1920); Report on the Fixation and Utilization of Nitrogen, p. 137 Bulletin 2041, U. S. War Dept. (1922).

A voltmeter, ammeter, and wattmeter connected in the primary circuit gave the power input and also the power factor. In the secondary circuit the potential across the arc was indicated with a Kelvin electrostatic voltmeter and the current with a milliammeter.

There was some inaccuracy in the smaller readings on the scale of the electrostatic voltmeter and consequently the voltage (used in evaluating

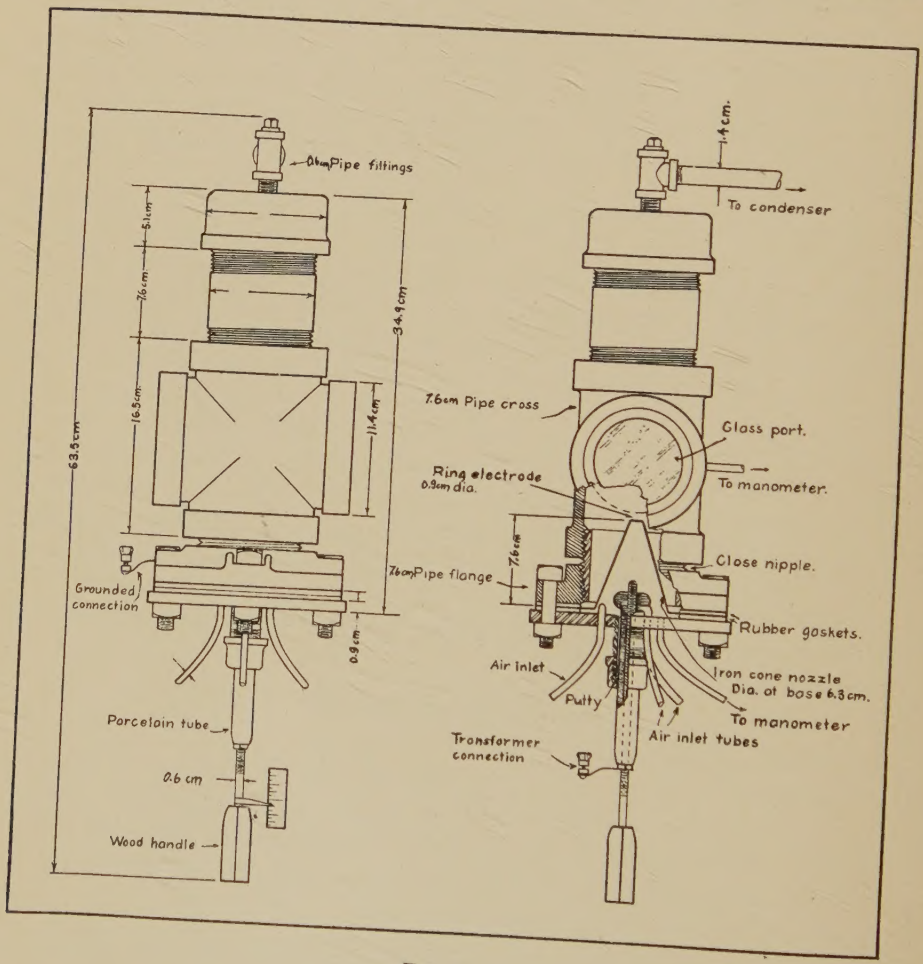

FIG. 1
Arc Furnace

yields) across the arc was calculated from the milliammeter readings, the power factor and the net wattage obtained by deducting the transformer loss from the total wattage indicated by the wattmeter in the primary circuit.

(b) *The Arc Furnace*

The arc furnace shown diagrammatically in Fig. 1 was selected because it gave a good yield of fixed nitrogen. The essential parts were an upper elec-

trode (which was grounded) shaped like a hollow frustrum of a cone, a lower centrally located rod electrode and gas inlet pipes. The gas entered through these pipes at a point slightly above the base and was forced with a whirling motion through the upper electrode. This motion of the gases spread the arc flame and also brought the cold air in very close contact with it; in fact, the arc, thus produced, might be regarded as somewhat similar to that of the Schönherr furnace. The central rod electrode was provided with a screw thread to permit the adjustment of the distance between the electrodes. The furnace enclosure was made largely from 7.6 cm. (3 inch) standard iron pipe fittings and could easily be taken apart. The upper electrode was fastened on a collar and this bolted between the flanges, see Fig. 1. The lower rod elec-

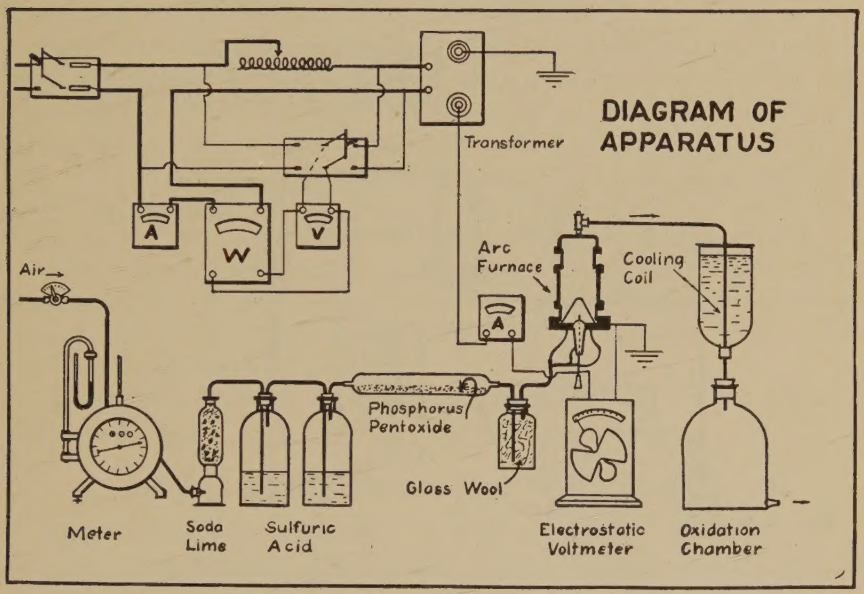

FIG. 2

trode was insulated from the remainder of the furnace by means of a porcelain tube set in stiff putty in a pipe bushing which was screwed into the base plate. The gas inlet pipes were 0.63 cm. (1/4 inch) copper tubes fitted tightly into the base plate. They were spaced 120° apart and were equally distant from the central electrode. The gas was given a rapid whirling motion by the nozzle-shaped ends of the inlet tubes which directed the flow tangentially against the frustrum-shaped electrode. A glass window in the side of the furnace permitted observation of the upper part of the arc at all times. Two other openings in the furnace allowed the necessary connections with pressure manometers to give the gas pressure below and above the upper electrode.

This laboratory arc furnace gives under proper conditions, an efficiency of 58 grams of fixed nitrogen (as HNO_3) per kilowatt hour, an efficiency near that obtained in commercial practice.

(c) *The Gas Apparatus*

The gas apparatus served two functions: first, to condition and measure the gas before it reached the arc; and second, to absorb the products formed by the action of the arc. Most of the gases were supplied from tanks under considerable pressure, needle valves being used to regulate the flow. The mixtures of nitrogen and oxygen were measured by passing them through the usual wet type of gas meter. The corrosive gases were passed through an all-glass flow meter to determine the volume. When necessary, moisture was removed from the gas by passing it first through concentrated sulfuric acid and then over phosphorus pentoxide.

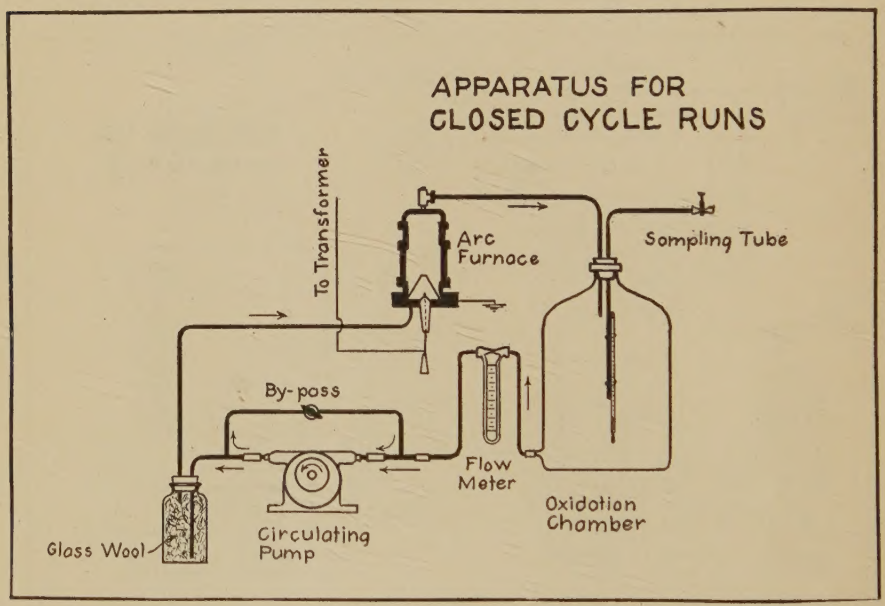

FIG. 3

After leaving the arc, the gas was conducted through a water-cooled glass condenser and then into a five-liter aspirator bottle (hereafter designated as the *oxidation* chamber) in which a considerable portion of the cooled nitric oxide was oxidized to nitrogen peroxide.

The general arrangement of the electrical equipment, furnace, and gas apparatus is shown in Fig. 2.

The apparatus just described was used when the gas was passed but once through the arc, a procedure which is here designated as a *direct run.* In other experiments, the gas was confined in a closed system and circulated repeatedly through the arc, here designated as a *closed cycle run.* A 15-liter bottle served as a gas reservoir and was connected in a closed circuit with the arc furnace, the flow meter and a small "Cenco" positive-acting rotary pump. The pump was equipped with a by-pass or shunt. See Fig. 3. By varying the

rate of flow of the gas through the by-pass the desired velocity of the gas through the closed cycle was easily controlled.

(d) *Methods of Analysis.*

The gas leaving the oxidation chamber was sampled in one or more different ways, namely: by vacuum flasks or by an absorption train. The vacuum flasks were round-bottom pyrex flasks, some 500 cc. and some 2000 cc. capacity, with narrow necks fitted with carefully ground stop-cocks. The oxides of nitrogen in the sample were absorbed in an excess of tenth-normal, carbonate-free sodium hydroxide. The excess of alkali was titrated to neutrality with standard acid using para-nitrophenol as an indicator. This procedure was checked against that used by the U. S. Government[1] at Nitrate Plant No. 1, and by the Devarda reduction method.

The absorption train consisted of 6 hydrometer jars 5 cm. wide and 50 cm. long each fitted with inlet and outlet tubes and connected in series with the oxidation chamber. The jars contained a known amount of standard alkali mixed with hydrogen peroxide solution (3%). Glass wool was placed in the jars to break the gas into small bubbles and thus bring about complete absorption of the oxides of nitrogen. At the end of a run the excess of alkali was titrated with standard sulfuric acid using methyl red as the indicator.

When the absorption train was used to evaluate the fixation of reduced pressure runs, a "Cenco" rotary pump was placed in the gas line as a "booster pump" just ahead of the absorption towers so that absorption could take place under atmospheric pressure.

The results obtained using the vacuum flasks and the absorption train were concordant.

Effect of Velocity of Gas through the Arc upon the Yield

In starting experimental work on the formation of nitric oxide with an arc furnace, a determination must be made of the influence of the velocity of air through the arc upon the per cent by volume of nitric oxide and the yield per kilowatt hour. In this investigation, the work was extended to include the mixtures of nitrogen and oxygen varying from the ratio found in air to that of "invert air" (4 vols. oxygen to 1 vol. nitrogen). The composition of gas for each experiment was checked by the analysis of a composite sample extending over the entire run.

The relation between the velocity of air and the electrical values and yield is shown by the data in Table I, also by Fig. 4. The almost constant amperage is due to the reactance in the circuit.

An inspection of Table I and Fig. 4 shows that with constant current and distance between the electrodes, the concentration of nitric oxide for any given mixture decreased with the velocity; and within the limits tried, 200 to 600 liters per hour, the concentration of nitric oxide was a linear function of the velocity.

[1] J. Ind. Eng. Chem., **11**, 745 (1919).

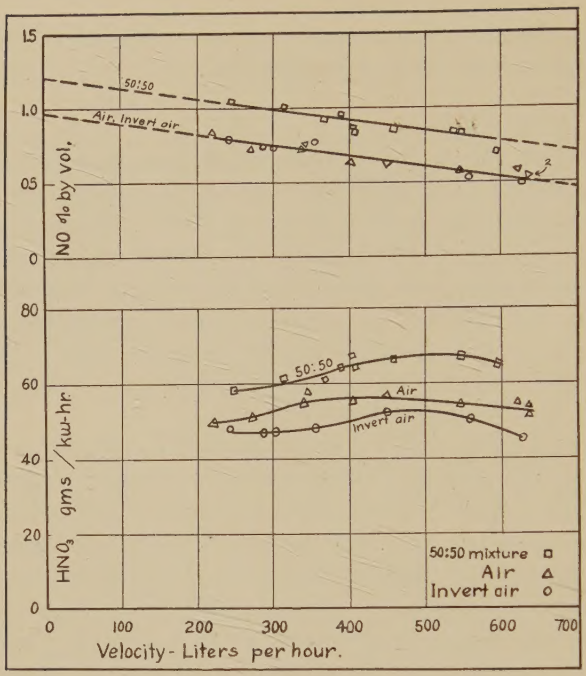

FIG. 4 (upper part)

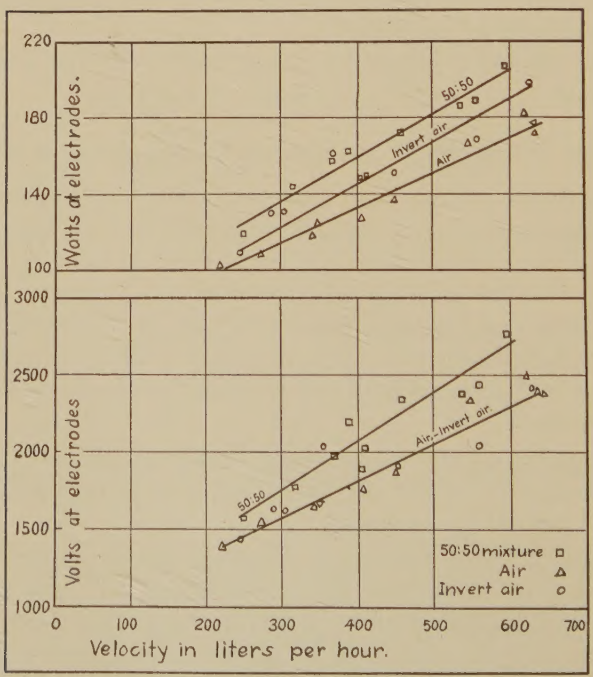

FIG. 4 (lower part)

FIG. 4. (2 parts—upper and lower). Direct Runs on Mixtures of Oxygen and Nitrogen; Arc at Atmospheric Pressure; Velocity of Gas thru Arc, 200 to 600 Liters per Hour.

The yield of fixed nitrogen reached a maximum value at an intermediate velocity which depends somewhat on the composition of the gas and its rate of flow. The maximum yields occurred at velocities varying from 350 to 500 liters per hour; or 2000 to 3000 liters per kilowatt hour. These yields at these velocities could be secured only with a current of 90 milliamperes. Doubling the current gave an increase in the concentration of nitric oxide but a decrease in the yield per kilowatt hour. Several runs were made using a current of 30 milliamperes with various gas mixtures at a velocity of approximately 340 liters per hour. The results are recorded in Table II.

TABLE I

Direct Runs on Mixtures of Oxygen and Nitrogen; Arc at Atmospheric Pressure; Velocity of Gas, 200 to 600 Liters per Hour

Expt. No.	At electrodes: Current milli-amperes	At electrodes: Approx-imate voltage	Watts, corrected for trans-former losses	Velocity of gas thru arc. Liters per hr. Stand. cond.	Nitric oxide, per cent by volume	Oxygen, per cent by volume	Nitrogen, per cent by volume	Nitric acid (HNO_3) gms. per kw.-hr.	Watt-hours required as heat of formation of nitric oxide
Air									
64f	95	1410	104	220	0.84	air	air	50.0	2.06
64g	92	1550	109	273	0.73	"	"	51.5	2.23
64h	92	1660	119	339	0.72	"	"	56.0	2.65
64e	94	1680	125	342	0.76	"	"	58.6	2.91
75	95	1710	128	352	0.72	"	"	56.0	2.84
64i	93	1780	127	404	0.63	"	"	56.0	2.82
64j	93	1880	137	448	0.62	"	"	57.3	3.12
64k	90	2340	167	546	0.59	"	"	54.4	3.61
64n	90	2500	182	622	0.57	"	"	55.5	4.01
64l	89	2400	172	632	0.52	"	"	54.4	3.71
64m	89	2400	177	634	0.52	"	"	52.1	3.67
Approx. 50% N_2. 50% O_2									
66	92	1590	120	241	1.05	43.48	55.47	59.0	2.81
64	95	1790	144	314	1.00	49.50	49.50	61.8	3.54
63	94	1980	158	371	0.93	44.03	55.04	61.4	3.85
64b′	90	2200	163	390	0.96	48.72	50.32	64.7	4.18
64c	93	1900	148	404	0.87	45.76	53.37	67.0	3.93
64b	90	2020	150	407	0.84	48.18	50.98	64.0	3.81
64c′	89	2340	172	461	0.87	48.07	51.06	65.8	4.48
65	93	2380	187	535	0.84	39.58	59.58	67.5	5.02
67	91	2450	189	546	0.83	49.59	49.58	67.2	5.05
68	89	2780	208	593	0.70	49.65	49.65	65.6	5.42
Invert Air									
69	93	1430	110	240	0.80	78.60	20.60	48.7	2.13
70	93	1640	130	289	0.75	79.23	20.02	47.2	2.44
73	94	1630	132	302	0.74	73.63	25.63	47.4	2.48
73b	91	2040	162	357	0.78	78.61	20.61	48.5	3.10
71	94	1910	151	450	0.63	76.68	22.69	53.2	3.19
72	96	2050	169	561	0.54	78.73	20.73	50.6	3.40
74	92	2420	199	628	0.52	78.74	20.52	45.8	3.63

TABLE II

Direct Runs on Mixtures of Oxygen and Nitrogen: Arc at Atmospheric Pressure: Current 30 Milliamperes: Gas Velocity 340 Liters per Hour

Expt. No.	At electrodes Current milli-amperes	At electrodes Approx-imate voltage	Watts corrected for transformer I^2R loss only	Velocity of gas thru arc. Liters per hour. Stand. cond.	Nitric oxide per cent by volume	Oxygen per cent by volume	Nitrogen per cent by volume	Gms. Nitric Acid (HNO_3) per kw.-hr. (Approximate)
Air								
121	30	2400+	80	351	0.28	Air	Air	35
126	30		80	344	0.28	"	"	34
126′	30		80	344	0.32	"	"	39
Approx. 50% O_2, 50% N_2								
122	30	2400+	80	328	0.33	49.0	50.7	38
Invert Air								
123	30	2400+	80	302	0.13	79.6	20.3	14
124	30		80	322	0.09	81.5	18.4	10
125	30		80	336	0.14	77.5	22.4	16
127	30		80	344	0.11	77.0	22.9	13
127′	30		80	344	0.15	77.0	22.8	18

The data of Table I (and Fig. 4) also show that air and invert air gave the same concentration of nitric oxide at the corresponding velocities. Furthermore, under similar conditions, the 50-50 mixture gave the greatest concentration of nitric oxide. The *relative increase* in the nitric oxide content due to oxygen enrichment depended upon the velocity of the gas at which the comparison was made. At 230 liters per hour there was a gain of 25 per cent; at 550 liters the gain was 40 per cent. This effect of velocity suggests an explanation for the discordant results reported by various investigators for the increase in nitric oxide content resulting from oxygen enrichment of the gas supplied to an arc. An idea of the wide divergence of these results may be obtained from the following quotation from Norton[1]: "McDougal and Howles, in 1900, when using a small experimental plant, nearly doubled the actual yield of NO by changing from air to the mixture of equal volumes, and obtained a concentration of 8.5 per cent NO in the cool gases. The fact of a very pronounced increase in the yield is confirmed by Lepel, by Kowalski and Moscicki (who secured an increase of 50 per cent), by Briner and Durand (37 per cent), by Le Blanc and Muranen (29 per cent), and by Guye (16 to 60 per cent)."

The data (Table I) on the yields per kilowatt hour for air and the 50:50 mixture, show that the enrichment with oxygen, gave an increase varying from 14 to 25%, the latter figure being for a velocity of 600 liters per hour. A comparison of the yields with the 50:50 mixture and with invert air shows a gain varying from 21 to 32%. The maximum increases in yield from the use of the 50:50 gas are in general accord with the mass action law. Fig. 4

[1] Norton: Bulletin No. 52, Special Agent Series, U. S. Dept. of Commerce and Labor, p. 84.

brings out the fact that the wattage of the arc was not kept uniform for the different mixtures at any one velocity and consequently close comparisons with respect to the mass law are hardly permissible.

The appearance of the arc changed gradually as the rate of gas flow was increased. At 225 liters per hour (current of 0.1 to 0.2 amperes), a yellow luminous arc was obtained while at 600 liters per hour the steady, luminous zone almost completely disappeared, a blue sparking arc taking its place.

Direct Runs at Reduced Pressure

In the runs at reduced pressures the arc was operated in practically the same manner as in the direct runs at atmospheric pressure. Two stop-cocks

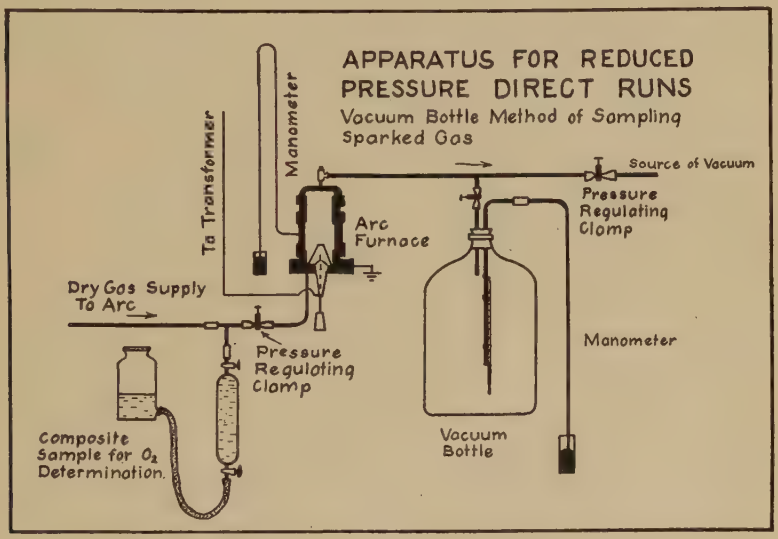

FIG. 5

were inserted in the gas line; one immediately before the arc furnace and the second after the exit from the furnace. The tube from the latter stop-cock was connected to a large capacity vacuum pump. The arrangement of the apparatus is shown in Fig. 5.

The voltage across the arc decreased with the reduction of pressure. The most noticeable change, however, was in the appearance of the arc itself. Under normal pressure and an air velocity of 340 liters per hour, the arc appeared to be made up of two intermixed parts, one was a bright luminous zone which extended from the rod electrode to about one-half inch above the upper electrode; the other consisted of spark-like streamers that played with a rotary motion between the electrodes. As the pressure was reduced, the luminous zone rapidly disappeared and the spark-like streamers became more numerous, slightly distorted and of a more blue color. The luminous zone disappeared entirely with further reduction in pressure and the arc had the appearance of a spark or brush discharge.

Samples of the gas were taken at the exit of the furnace by the vacuum flask method. Large bottles, 20 liters capacity provided with tightly fitting stoppers with stop-cocks, were substituted for the vacuum flasks previously mentioned.

The experimental data for the reduced pressure runs are reported in Table III and graphically represented in Fig. 6.

TABLE III

Direct Runs on Mixtures of Oxygen and Nitrogen: Arc at Reduced Pressures

Expt. No.	Pressure in arc chamber mm. of Hg.	At Electrode: Current milli-amperes	At Electrode: Approximate voltage	Watts corrected for transformer losses	Velocity of gas thru arc. Liters per hr. stand. cond.	Nitric oxide per cent by volume	Oxygen per cent by volume	Nitrogen per cent by volume	HNO_3, gms. per kw.-hr.
Air									
92	130	98	800	66	206	0.24	Air	Air	21.6
93	149	96	950	65	219	0.20	"	"	19.0
100	298	96	1120	80	236	0.36	"	"	30.0
86	455	95	1200	85	196	0.62	"	"	39.9
88	451	97	1180	84	201	0.58	"	"	39.0
105	594	93	1170	86	204	0.46	"	"	42.6
64f	768	95	1410	104	221	0.84	"	"	50.0
Approx. 50% O_2, 50% N_2									
96	140	99	900	64	200	0.17	44.92	54.91	15.5
97	147	97	925	62	235	0.20	46.90	52.90	21.8
98	130	96	—	61	203	0.22	48.39	51.39	20.8
99	294	97	1050	76	227	0.38	46.81	52.81	31.5
89	452	94	1150	80	223	0.67	56.67	42.66	53.0
101	460	94	1130	81	245	0.54	48.73	50.73	45.4
104	599	93	1270	101	208	0.41	48.80	50.79	49.7
66	760	92	1590	120	241	1.05	43.48	55.47	59.0
Invert Air									
95	145	97	940	59	239	0.13	76.94	22.94	14.9
91	453	96	1100	85	212	0.60	77.70	21.70	42.2
90	460	96	1125	86	219	0.61	74.69	24.70	43.8
69	772	93	1430	110	250	0.80	78.60	20.60	48.7

The results showed that there was a gradual decrease both in the concentration of the nitric oxide and the yield per kilowatt hour as the pressure was reduced. At corresponding pressures, the 50:50 mixture gave a greater yield than the other mixtures.

An important difference between the direct runs made at atmospheric pressure and those at reduced pressure was the length of time required for the passage of the gas particles through the furnace. For a given gas flow (in these experiments, 200-250 liters per hour), the velocity of the particles through the arc chamber increased with the reduction in pressure. At a pres-

sure of 150 mm., the particles were swept through the furnace at a velocity nearly 5 times greater than when the same quantity of gas was passed through at 760 mm.[1]

The results reported here are of interest in connection with the work of Haber and Köenig[2] with alternating current arcs at pressure around 100 mm.

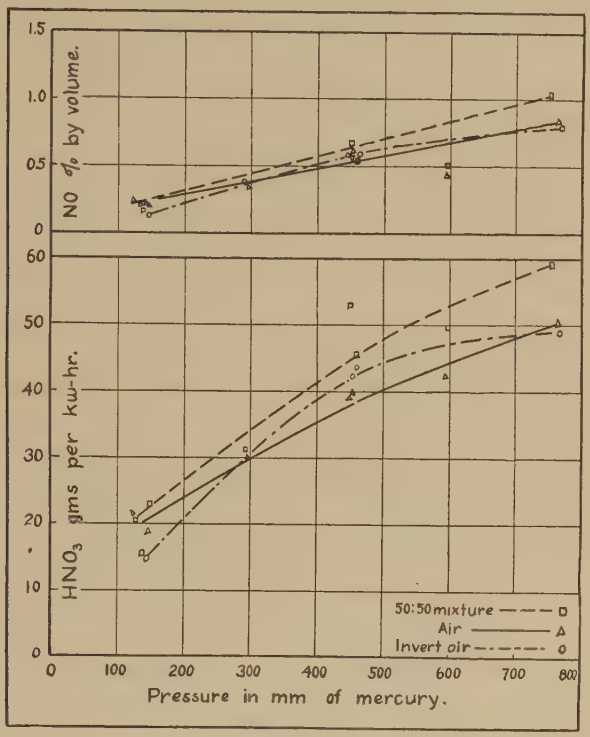

FIG. 6

Direct Runs at Reduced Pressures, (100 to 760 mm.) upon Mixtures of Oxygen and Nitrogen; Gas Velocity 200 liters per hour; Arc Current, 95 milliamperes.

The concentration of nitric oxide obtained depended upon composition of the mixture of nitrogen and oxygen used; 9.8% from air, 14.5% from the 50:50 mixture and 12.5% from "invert air". These high values were obtained, however, with a gas flow of only a few liters per hour. The writers have not obtained any results *indicating that a decrease in pressure may be utilized in securing a greater efficiency in yield by the arc process.*

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[1] Additional experiments have been made by Mr. P. G. Cohen in this laboratory, reducing the rate of flow of gas through the arc as the pressure was diminished in order to keep the velocity of the particles of gas through the arc constant. The data show that the yield decreased in a manner closely analogous to the results reported above. These additional results will be offered for publication at an early date.

[2] Haber and Köenig: Z. Elektrochem., **13**, 725 (1907).

Closed Cycle Experiments

(a) *The Experimental Part*

The closed cycle runs were made at atmospheric pressure with a power input ranging from 65 to 200 watts. In most cases, the rate of flow of gas was that required to give the maximum yield of fixed nitrogen with air at atmospheric pressure. Closed cycle experiments were conducted on a series of mixtures of nitrogen and oxygen, the content of the latter substance being varied from 20% to 85% by volume. The purpose of these experiments was to determine the equilibrium concentration of nitric oxide obtained by passing the gas repeatedly through the arc. The combined nitrogen existed in the cooler parts of the apparatus largely as nitrogen dioxide. This substance is completely dissociated above 600° into oxygen and nitric oxide. Furthermore, the rate of dissociation is extremely rapid at higher temperatures and consequently the combined nitrogen was assumed to exist as nitric oxide within and in the immediate vicinity of the arc.

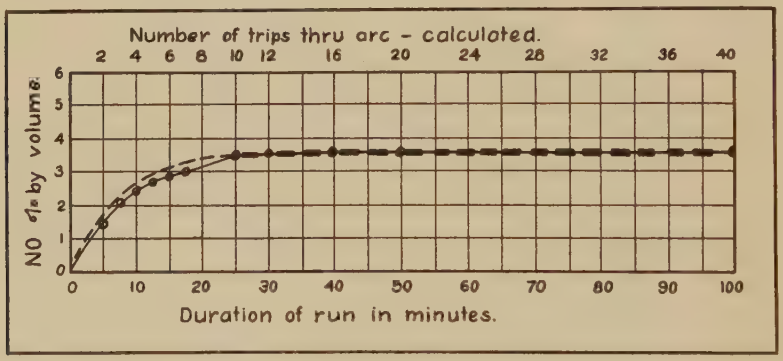
Number of trips thru arc - calculated.
2 4 6 8 10 12 16 20 24 28 32 36 40
NO % by volume.
0 1 2 3 4 5 6
0 10 20 30 40 50 60 70 80 90 100
Duration of run in minutes.

FIG. 7

Closed Cycle Runs at Atmospheric Pressure. Increase of Nitric Oxide with Successive Passages of Mixture thru the Arc at Velocity of 336 Liters per hour; Initial Mixture = Air.

Equilibrium was approached from either direction by obtaining the same final concentration of nitric oxide from mixtures initially containing, on one hand, no nitric oxide and on the other hand, an excess of this substance. The first closed cycle experiments were made to determine the rate of increase or decrease in the concentration of nitric oxide and the time required to reach equilibrium. The change in the nitric oxide content with successive passages through the arc was followed by taking samples at time intervals corresponding to those estimated for the successive cycles. In experiments 61d and 61e, dry air was introduced to replace the gas removed for analysis. This small periodic dilution prolonged somewhat the time required to reach equilibrium. The dilution was reduced to a minimum by admitting the air into the gas line immediately preceding the arc furnace, thus subjecting the newly introduced gas to the action of the arc prior to diffusion. A correction for the dilution was obtained by making a second run under identical conditions without

sampling until the arc had been operated for 25 minutes. The results of these experiments are given in Table IV and graphed in Fig. 7, the values corrected for dilution being indicated by the dotted line. In the later runs, dilution attending sampling was avoided by allowing gas of approximately the same concentration to replace that withdrawn. The arc was continued in operation until there was no further change in the concentration of nitric oxide. The extremely slow rate of oxide formation with reduced current strength (30 milliamperes) is shown by the data of experiment 61g also included in Table IV.

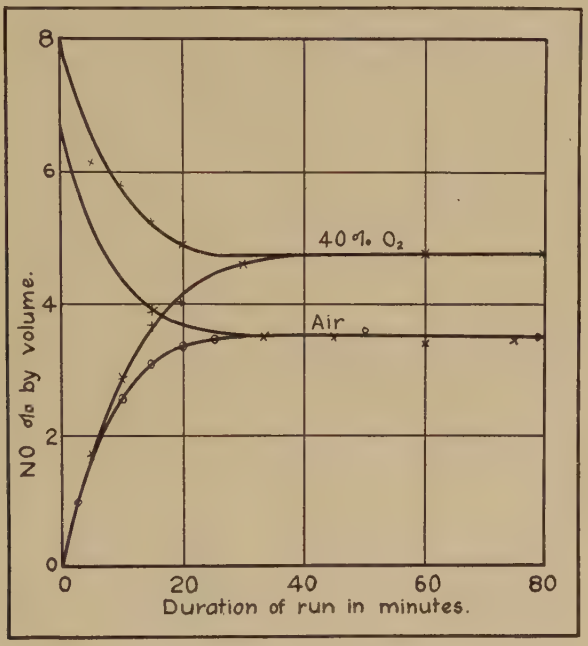

FIG. 8

Closed Cycle Runs at Atmospheric Pressure, approaching Equilibrium from both Directions. Velocity of Gas thru Arc, 330 Liters per Hour. Arc Current, 185 milliamperes.

Equilibrium was also approached from both directions using mixtures which had nearer the same total nitrogen and oxygen content; in one case no combined oxide was present, while in the other, the initial nitric oxide concentration was twice the final equilibrium value. Results obtained with mixtures containing different nitrogen-oxygen ratios are given in Table V and represented graphically in Fig. 8. The curves show that the same final concentration of nitric oxide was reached using gases initially free from, or containing an excess of this substance; also, that at a given time, the rate of decomposition was similar to the rate of formation of nitric oxide. Under these conditions, approximately 10 cycles through the arc were required to approach closely the equilibrium value, 80% of the final concentration of nitric oxide being obtained with about 5 cycles.

The next group of experiments were made expressly for the study of the application of the law of mass action to the formation of nitric oxide in the high tension arc. Here the careful determination of the final equilibrium concentrations was the essential factor, the rate of oxide formation being of secondary importance. The equilibrium constant for the reaction, $N_2 + O_2 = 2NO$, was calculated in accordance with the mass action law as follows (concentrations expressed as per cent by volume):

$$K = \frac{(NO)^2}{(N_2) \times (O_2)}$$

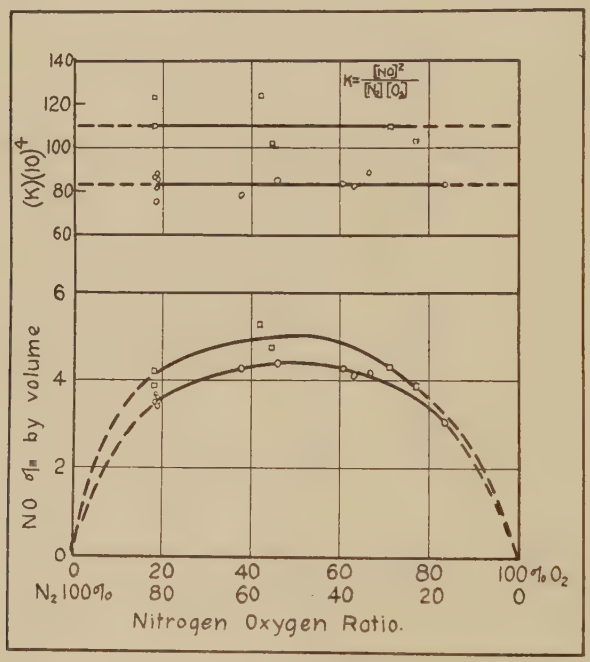

FIG. 9

Equilibria from Closed Cycle Runs.
o = values for arc currents of 100 to 160 milliamperes.
□ = values for arc currents of 30 milliamperes.

These equilibrium runs were made with currents ranging from 30 to 190 milliamperes; the gas mixtures were varied in composition from air to "invert air". The results of these tests are given in Table VI and are shown graphically in Fig. 9. The values obtained for the equilibrium constant K were of the order of (80 to 200) (10^{-4}) and, for convenience, have been multiplied by the factor, 10^4. The values for experiments 51a, 51b, 52a, and 52b were omitted from the graph because a greater gas velocity was used than that necessary for the maximum yield in a direct run. A Thorardson transformer was used to supply the current of 30 milliamperes. The core loss of this transformer was not determined, and consequently the reported wattages are somewhat high. The slow rate of nitric oxide formation with this low current arc greatly prolonged the time required to reach equilibrium.

Table IV

Closed Cycle Runs at Atmospheric Pressure. Increase of Nitric Oxide with Successive Passages of Mixture through the Arc

Expt. No.	Minutes duration at time of sampling	At electrodes: Current milli-amperes	At electrodes: Approx-imate voltage	At electrodes: Watts corrected for transformer losses	Velocity of gas thru arc. (stand. cond.) Liters per hour	Nitric oxide, per cent by volume	Oxygen, per cent by volume	Nitrogen, per cent by volume	(K) (10^4)
61d	0	190	1240	177	336	0.00			
	2.5	191	1250	185	336	0.97			
	5.0	190	1250	182	336	1.55			
	7.5	191	1260	187	336	2.08			
	10.0	191	1280	188	336	2.44			
	12.5	191	1300	190	336	2.71			
	15.0	190	1300	190	336	2.87			
	17.5	190	1300	192	336	2.96			
	25.0	190	1320	192	336	3.54	19.03	77.43	85.1
61e	0	189	1230	178	336	0.00			
	10	189	1260	183	336		Not sampled		
	20	189	1300	189	336				
	25	188	1310	189	336	3.54			
	30	188	1310	194	336	3.54			
	40	188	1320	194	336	3.67			
	50	188	1350	200	336	3.63			
	100	188	1350	200	336	3.58	19.01	77.41	87.3
61g	0	30	2250	60+	325				
	10	30			325	0.73			
	20	30			325	1.43			
	30	30			325	1.81			
	40	30			325	2.33			
	50	30			325	2.58			
	70	30			325	3.28			
	90	30			325	3.77			
	130	30	2640	65+	325	4.21	18.70	77.10	123.0

+Approximate Values.

Table V

Closed Cycle Runs at Atmospheric Pressure, approaching Equilibrium from both Directions

Expt. No.	Minutes duration at time of sampling	At electrodes: Current milli-amperes	At electrodes: Approx-imate voltage	Watts corrected for transformer losses	Velocity of gas thru arc. (stand. cond.)	Nitric oxide, per cent by volume	Oxygen per cent by volume	Nitrogen per cent by volume	K (10^4)
61e See Table VII.									
114	0	190	1350	202	335	6.67			
	15	190	1350	202	335	3.92			
	33	188	1340	197	335	3.52			
	45	186	1330	188	335	3.52			
	60	185	1350	193	335	3.44			
	75	188	1320	197	335	3.49			
	90	185	1340	193	335	3.52	17.24	79.24	90.6
115	0	185	1370	192	330	0.00			
	5	184	1400	197	330	1.72			
	10	182	1380	182	330	2.90			
	15	185	1400	199	330	3.72			
	20	185	1440	207	330	4.05			
	30	184	1450	204	330	4.60			
	60	183	1410	197	330	4.78			
	90	183	1410	197	330	4.78			
	100	183	1410	197	330	4.78	35.61	59.61	107.0
116	0	185	1410	199	330	8.02			
	5	185	1410	199	330	6.13			
	10	188	1400	204	330	5.81			
	15	188	1430	209	330	5.21			
	20	188	1430	209	330	4.90			
	30	188	1470	214	330	4.78			
	60	188	1480	219	330	4.78			
	90	188	1480	219	330	4.78	40.61	54.61	103.5

TABLE VI

Closed Cycle Runs at Atmospheric Pressure: Evaluation of Equilibrium Constants

Expt. No.	Minutes duration at time of sampling	At electrodes: Current milli-amperes	At electrodes: Approx-imate voltage	At electrodes: Watts corrected for transformer losses	Velocity of gas thru arc. (stand. cond.) Liters per hour	Nitric oxide, per cent by volume	Oxygen, per cent by volume	Nitrogen per cent by volume	K (10^4)
	100 to 200 Milliamperes.								
49a	35	100	1500	109	328	3.60	19.00	77.40	88
49b	50	193	1300	145	328	3.48	19.06	77.46	82
51a	30	95	1850	143	634	3.39	19.10	77.50	78
51b	70	193	1500	202	634	3.64	18.98	77.38	90
52a	30	95	1600	114	478	3.54	19.03	77.43	85
52b	50	188	1200	152	478	3.48	19.06	77.46	82
54	30	183	1300	197	340	4.10	63.30	32.60	82
55	20	183	1400	224	331	4.20	61.10	34.70	83
57	30	186	1500	221	334	3.06	83.97	12.97	82
58	30	182	1400	221	334	4.15	66.92	28.93	89
59	40	184	1200	205	331	4.38	46.31	49.30	84
60	25	187	1450	221	331	4.21	38.00	57.80	78
61a	25	187	1350	187	328	3.34	19.13	77.53	75
61d	25	190	1320	192	336	3.54	19.03	77.43	85
61e	50	188	1350	190	336	3.63	18.99	77.38	88
	30 Milliamperes.								
61g	130	30	2640	65+	325	4.21	18.70	77.10	123
119	90	30	3000	70+	322	3.86	18.87	77.27	110
117	120	30	2800	75+	326	5.26	42.20	52.60	124
120	90	30	3000	80+	324	4.78	44.50	50.70	101
118	120	30	2800	75+	322	4.32	72.05	23.63	109
128	90	30	2800	80+	322	3.82	78.03	18.13	103

+Approximate Values.

(b) *Discussion of Closed Cycle Runs*

The rate of oxide formation experiments (Table IV and Fig. 7) afford interesting information concerning the fixation of nitrogen in the high tension arc. The data make possible the numerical calculation of the relative volumes occupied by the spark-like filaments or streamers in which the nitric oxide is formed and by the cooler gas (in the region between the electrodes) surrounding these filaments. The calculation of these relative volumes is based upon the relation of the concentration of the nitric oxide secured by a single passage of the gas through the arc to the concentration of the oxide at equilibrium. The method of calculation is brought out in the following example. In experiment 61d the nitric oxide concentration for the initial passage of air through the arc was 0.97 per cent; the equilibrium concentration, 3.55 per cent. The latter value is the NO concentration of the cooler gas which was in equilibrium with the gas coming from the filament at the particular tem-

perature at which the equilibrium was "frozen". By extrapolation from their experimental data, Nernst, Finckh and Jellinek[1] estimate the temperature corresponding to this concentration to be 3000° Abs.

In the initial passage through the furnace, the gas from the filament (3.55 per cent NO) was diluted with the air from the cooler zones which reduced the concentration of nitric oxide to 0.97 per cent. This means that out of every 100 cc. of gas which passed through the arc, 27.3 cc. passed through the filaments and 72.7 cc. through the adjacent cooler zones. In the second passage each 27.3 cc. of gas from the filaments (3.55 per cent NO) was cooled by mixing with 72.7 cc. of gas containing 0.97 per cent NO producing a concentration of 1.67 per cent NO. In the third exposure to the arc, each 27.7 cc. of 3.55 per cent gas from the filaments was diluted with 72.7 cc. of 1.67 per cent gas producing a concentration of 2.19 per cent NO. The content of nitric oxide for the succeeding passages may be calculated in a similar manner. The calculated and experimental values for the first 11 cycles are given in Table VII.

TABLE VII

Comparison of Observed and Calculated Nitric Oxide Concentrations for Successive Exposures to Arc

Cycle	Per cent NO (calc.)	Per cent NO (observed)	Per cent NO (observed, corrected for dilution attending sampling.)
1	—·—	0.97	0.97
2	1.67	1.55	1.70
3	2.19	2.08	2.20
4	2.56	2.44	2.60
5	2.83	2.71	2.90
6	3.02	2.87	3.10
7	3.17	2.98	3.30
8	3.27	——	3.40
9	3.35	——	3.50 From curve.
10	3.40	——	3.50
11	3.44	3.54	3.54

The calculated nitric oxide content at the successive cycles corresponds with the observed values indicating that the assumptions made are close to the truth.

Upon the basis of the preceding assumptions and calculations an estimate of the energy efficiency for the most effective operation of an arc can be made. The energy required is that necessary to heat the air in arc filament (only) from room temperature to 3000° Abs. plus the heat of formation in the nitric oxide produced. According to Lewis and Randall,[2] the molal specific heat for air, oxygen, nitrogen and nitric oxide, is best represented by the equation:

$$C_p = (6.5 + 0.001T)$$

[1] Nernst, Finckh and Jellinek: Z. anorg. Chem., **45**, 116, 126, (1905); **49**, 213, 229 (1906).

[2] Lewis and Randall: J. Am. Chem. Soc., **34**, 1128 (1912).

in which C_p is the molal specific heat in calories at constant pressure and T is the absolute temperature. This equation is based upon experimental data reaching to 2000° Abs.; consequently, its application to higher temperature involves an extrapolation. However, this is the best data available so far as the writers are aware. The calculation of the heat required to heat one mol of air from 293° to 3000° Abs. is made by the integration of the equation $Q = C_p dT$ between the limits corresponding to these temperatures.

$$Q = \int_{293}^{3000} (6.50 + 0.001T)\ dT$$
$$= 6.5\ (3000 - 293) + 0.001/2\ (3000^2 - 293^2)$$
$$= 22052 \text{ calories.}$$

In addition to heating the air, 0.0355 mol of nitric oxide is formed. The molal heat of formation of nitric oxide is −21600 cal.; to form 0.0355 mol requires 767 calories. The total heat required is therefore, 22052 + 767 = 22819 calories.

The best efficiency (yield per kw-hr.) secured with the arc used in this investigation was obtained in experiment 64e, previously reported in Table I. The data are as follows: air velocity, 342 liters per hour; arc current 94 milliamperes; power at the electrodes, 125 watts; and the concentration of nitric oxide produced 0.76 per cent. The equilibrium concentration of nitric oxide for these conditions is 3.55 per cent. Using these concentrations as a basis, the calculated air passing through the arc filament is 22.5 per cent of the total air going through the furnace, or 76.95 liters (3.44 mols) per hour. The heat required for the heating of this quantity of air from 293° Abs. to 3000° Abs. is, 3.44 × 22819 = 78497 cal. The actual experimental energy was 125 watt hours, which is equivalent to 107500 calories. Hence, (78497 ÷ 107500) (100) or 73 per cent is the thermal efficiency obtained in this experiment in which the yield was 58 grams of nitric acid per kilowatt hour.

The value of the equilibrium concentration also permits the calculation of the maximum concentration of nitric oxide to be secured by a single passage of the gas through the arc. The velocity of decomposition of nitric oxide has been investigated by Jellinek[1] for the temperature range 689°C. to 1750°C. From this reaction constant and the equilibrium constant for the reaction, the reaction constant for the formation of nitric oxide can be determined. From these data the rates of formation and of decomposition of nitric oxide in any given mixture can be calculated[2]. The calculated time required for the decomposition at 1900° Abs. of 40 per cent of the nitric oxide present in an air mixture at 1 atmosphere containing initially twice the amount of this substance that will be present when equilibrium is established, is 2-1/2 minutes. At 1773° Abs. the time required for this amount of decomposition is 21

[1] Jellinek: Z. anorg. Chem., **49**, 263 (1906).

[2] For details concerning the formulations and method of calculation, the reader is referred to pp. 134, Bulletin 2041, U. S. War Dept.; Report on the Fixation and Utilization of Nitrogen.

minutes. The gas from the arc zone should surely be cooled quickly to at least 1900° Abs. to "freeze" the equilibrium. Below this temperature the rate of decomposition will be sufficiently slow that the gas may be cooled less rapidly without appreciable loss of combined nitrogen. In suddenly chilling the gas from the arc filament from 3000° Abs. to 1900° Abs. the cold air will be heated to 1900° Abs. The amount of heat absorbed in heating one mol of air from 293° Abs. to 1900° Abs. may be estimated as follows:

$$Q = \int_{293}^{1900} (6.5 + 0.001T)\, dT$$
$$= 6.5\,(1900 - 293) + 0.001/2\,(1900^2 - 293^2)$$
$$= 12{,}207 \text{ cal.}$$

Previous calculations show that 22052 cal. are required to heat 1 mol of air from 293° Abs. to 3000° Abs. Then

$$22052 - 12207 = 9845 \text{ cal.}$$

the heat to be removed in cooling 1 mol of the gas from the arc filament to 1900° Abs. And $9845 \div 12207 = 0.806$, the number of mols of cold air required to cool 1 mol of the gas from the filament. If the gas from the filament contains 3.55 per cent of nitric oxide (the equilibrium value) and is cooled without further decomposition by adding 0.806 mol of cold air, the cooled gas will contain 1.91 per cent of nitric oxide. This is the calculated maximum concentration of this substance that can be secured from an arc with cooling as effective as that accomplished in this investigation. This value closely approximates the maximum concentration of nitric oxide which has been secured in commercial practice with good energy efficiency, viz. 1.8 per cent by the Schönherr-Hesselberger furnace.

The equilibrium concentrations (closed cycle runs) for the different amperage arcs indicated that the "freezing" of the equilibrium by mixing with cold air in the furnace was very effective. From Jellinek's data the estimated time for the decomposition at 3000° Abs. of 40 per cent of the nitric oxide in an air mixture containing 200 per cent of the equilibrium concentration of this substance, is 1.2×10^{-5} seconds. The writers realize that this reaction velocity was obtained by extrapolation from experimental data secured at lower temperatures. Nevertheless, the rapidity with which the equilibrium was "frozen" with this type of whirling arc is almost incredible.

Many cycles were required to secure equilibrium with currents of 30 milliamperes. This indicates that the volume of the gas passing through the filament was small compared to the volume passing through the surrounding cooler zones, being of the order of a fraction of a per cent. The meagre data so far secured hardly justify the calculation of the actual volume of the filament. However, the results show that a reduction in the arc current strength decreases the effective volume of filament. Furthermore, there is no indication that decrease of current is necessarily attended by a change of the average kinetic energy of the particles in the filament.

The closed cycle experiments furnish trustworthy data (see Tables V and VI) concerning the application of the law of mass action to the fixation of

atmospheric nitrogen in the high tension arc having good energy efficiency. The curves in Fig. 9 show in each case that the concentration of nitric oxide at equilibrium increases in a regular manner to a maximum value as the volumes of nitrogen and oxygen forming the mixture become equal. Furthermore, the consistent values for the equilibrium constant for a series of experiments at a given current strength are in close accord with the mass action law. The difference in the values of the equilibrium constants for arcs of different current strengths is due to the "freezing" of the equilibrium at different temperatures. The writers have not obtained thus far any evidence with the experiments carried out, of any deviation from the mass action law due to any special "electrical effects".

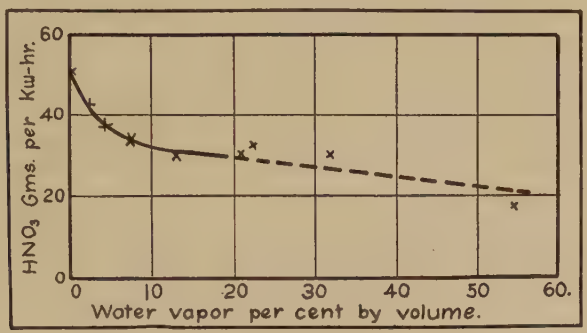

FIG. 10
The Effect of Water Vapor. Direct Runs at Atmospheric Pressure.

The Effect of Water Vapor

In the arc fixation of nitrogen in commercial quantities the oxygen-nitrogen mixture is simply air. Since the atmosphere contains moisture, information regarding its effect on fixation was determined for mixtures of air and water vapor in which the moisture content ranged from 2 to 50% by volume. The results are given in Table VIII and Fig. 10. In this series of experiments the arc furnace was inverted to prevent short-circuiting the high tension electrode due to condensation after passing through the arc of water from mixtures high in moisture.

The values for experiments with a moisture content as high as fifteen per cent are accurate, but the precision is somewhat less in the runs containing a greater amount of water vapor because of a tendency toward premature condensation of the moisture. Ample precautions were taken in the analyses to prevent any loss of fixed nitrogen due to a film of moisture on the walls of the apparatus. In order to carry out the experiments with the greatest precision, the entire furnace should be inclosed in a thermostat at a temperature somewhat above the dew point of the air-water mixture used. The authors have not yet had the opportunity to arrange an apparatus of this sort. Consequently, the experiments made thus far with higher percentages of water vapor may be somewhat in error.

These findings show that even with 2.6% moisture, which corresponds to 100 per cent humidity at 22°C., the yield was reduced to 42.1 grams of nitric acid per kilowatt hour which is a 25% decrease in production. Evidently a small amount of moisture may cause a very appreciable decrease in yield.

TABLE VIII

The Effect of Water Vapor

Direct Runs at Atmospheric Pressure on Moist Air

Expt. No.	Current Milli-amperes	Approx. voltage	Watts corrected for transformer losses	Velocity of gas thru arc. Liters per hour. (Stand. cond.)	Water vapor per cent by volume	Nitric oxide per cent by volume	Gms. HNO_3 per kw.-hr.
33	96	1740	136	2.6	2.6	0.56	42.1
34	97	1700	136	4.4	4.4	0.49	37.5
35	97	1810	151	7.5	7.5	0.47	33.8
36	96	1810	151	13.7	13.7	0.39	30.7
30	94	1720	129	20.8	20.8	0.34	30.2
29	94	1710	128	21.9	21.9	0.35	32.7
38	96	1680	141	32.0	32.0	——	30.2
39	92	——	153	54.3	54.3	0.136	18.0

Acknowledgment

Grateful acknowledgment is made to the E. I. du Pont de Nemours and Company for the grant of a fellowship which made possible this investigation.

Summary

1. A satisfactory laboratory arc furnace with good energy efficiency has been constructed.

2. A high gas velocity favored a high yield of fixed nitrogen per kilowatt hour but gave a lower per cent by volume of nitric oxide. Excessively high air velocities gave a low output in respect to both yield and concentration of fixed nitrogen.

3. The use of reduced pressure (with a gas velocity suitable for a good yield of fixed nitrogen at atmospheric pressure) gave a decrease both in the concentration of nitric oxide and in yield of fixed nitrogen per kilowatt hour.

4. A study has been made of the equilibria obtained with various mixtures of nitrogen and oxygen using a high tension arc with different amperages. The results show that the mass action law applies to the equilibria obtained. The temperatures at which the equilibria were "frozen" show that the cooling from the whirling arc is very efficient.

5. A method has been given which permits the calculation of the concentration of nitric oxide resulting from repeated exposures of a nitrogen-oxygen mixture to a high tension arc.

6. A value, based upon experimental data, has been given for the theoretical maximum concentration of nitric oxide that may be obtained with an arc, at an energy efficiency equivalent to 60 grams of nitric acid per kilowatt hour, for air supplied at room temperature and atmospheric pressure.

7. The presence of water vapor in the air supplied to the arc reduced both the yield and the concentration of the nitric oxide.